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(21) International Application Number: PCT/NL  (22) International Filing Date: 14 March 2000 (  (30) Priority Data: 1011580 17 March 1999 (17.03.99)  (71) Applicant (for all designated States except US): ENGINEERING B.V. [NL/NL]; Beunkdijk 11, 1 NZ Aalten (NL).  (72) Inventor; and (75) Inventor/Applicant (for US only): BEELE, Johanne [NL/NL]; Beunkdijk 11, NL-7122 NZ Aalten (NL)  (74) Agent: HOOIVELD, Arjen, Jan, Winfried; Arnold & Sweelinckplein 1, NL-2517 GK The Hague (NL).	BEEL NL-712 es, Alfra -).	BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AT, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  Published  With international search report.  Before the expiration of the time limit for amending the
(54) Title: LUMINESCENT COATING WITH A BASE (57) Abstract	OF A	WATER-BORNE POLYURETHANE DISPERSION
A luminescent coating comprising: a luminescent pig the group comprising calcium, strontium and barium, or on	the oth from th	of matrix formula MAl <sub>2</sub> O <sub>4</sub> , wherein M is at least one metal selected from her hand of matrix MAl <sub>2</sub> O <sub>4</sub> , wherein M is a multitude of metal elements, he group consisting of calcium, strontium and barium and a water-borne

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# LUMINESCENT COATING WITH A BASE OF A WATER-BORNE POLYURETHANE DISPERSION

The present invention relates to a luminescent coating with a base of a water-borne polyurethane dispersion.

More particularly, the invention relates to a luminescent coating comprising: a luminescent pigment of matrix formula MAl<sub>2</sub>O<sub>4</sub>, wherein M is at least one metal selected from the group comprising calcium, strontium and barium, or on the other hand of matrix MAl<sub>2</sub>O<sub>4</sub>, wherein M is a multitude of metal elements, comprising magnesium and at least one element selected from the group consisting of calcium, strontium and barium and a water-borne polyurethane binder dispersion.

A luminescent coating of this kind is known from US-A-5,665,793. According to said publication, a suitable amount of a paint containing a colour pigment is added to the aforesaid luminescent coating. This paint mixture is used as a roadway marking coating having enhanced luminescent properties.

The luminescent pigments and the water-borne polyurethane binder dispersions from said publication US-A-5,665,793 are considered to be incorporated in the present application, as are the composition ratios mentioned therein.

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The aforesaid luminescent pigments are sensitive to moisture and water. When luminescent pigments come into contact therewith, a heat-emission reaction results, which makes the coating unsuitable in use. This problem is overcome by diluting a suitable polyurethane dispersion as already recognized in the aforesaid patent with another paint which does not contain such watersensitive pigments.

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Another solution which is well-known for screening said luminescent pigments is to cover them with a protective layer.

- 5 It is an object of the present invention, however, is to provide a luminescent coating as such, which is not mixed with any other coating such as the paints provided with the new pigment which are known from the aforesaid US patent. Another object of the invention is to provide a coating which can be applied in minimum film thicknesses having sufficient luminescent power. Such film thicknesses can for example range between 15 and 30 μm, preferably they are about 10 μm.
- Another object of the present invention is to provide a suitable dilutant, so that a luminescent coating is obtained which is capable of being sprayed.

The problem of the coating referred to in the
introduction is that sagging occurs in the form of a
two-phase system after a period of rest. The pigments
form the heaviest fraction and they will migrate under
the lighter water-borne polyurethane dispersion
fraction. This makes the coating unsuitable for use.

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Surprisingly, this problem is overcome by adding a sagging additive in a low amount of 0.5 - 10 % by weight to the aforesaid coating. As a result, the luminescent pigments will remain suitably dispersed for a longer period of time, even after a prolonged period of rest of the coating.

Preferably, the anti-sagging additive is a hydrophobic pyrogenous silica. Said anti-sagging has appeared to be highly suitable for forming a permanent dispersion of the aforesaid luminescent pigments in a water-borne polyurethane dispersion.

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A preferred embodiment of the luminescent coating according to the invention consists of:

- 40 80 % by weight of water-borne polyurethane binder dispersion;
  - 19.5 59.5 % by weight of luminescent pigment;
  - 0.5 10 % by weight of anti-sagging additive.

The hydrophobic pyrogenous silica as the anti-sagging additive is preferably an AEROSIL®, which is marketed by the firm of Degussa.

Besides using the anti-sagging additive, it is advantageous to use an additive in the form of a

15 dispersion additive in an amount of 0.1 - 5 % by weight. This dispersion additive will further enhance the dispersion quality by preventing any flocculating activity of the luminescent pigments and keeping the anti-sagging additive dispersed. Preferably, the

20 dispersion additive is DISPERBYK\*, which is marketed by the firm of Byk Cera.

Preferably, the luminescent coating that is obtained is capable of being sprayed. To this end the invention provides a coating diluted with N-methyl-2-pyrrolidone. A preferred suitable dilution is N-methyl-2-pyrrolidone and water in a weight ratio of 1 : 12.

A preferred formula of the luminescent coating according to the invention is defined hereafter in Table 1.

TABLE 1

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Base materials	Туре	Supplier	Parts by weight
NeoRez R974	Binder dispersion	Zeneca Resins	63.31
RM 4456	Thickener	Stahl Holland	0.55
LLA 1698	Flow additive	Stahl Holland	0.1
Byk 028	Defoaming agent	Byk Cera	1.09
Disperbyk	Dispersion additive	Byk Cera	1.11
Aerosil R 972	Anti-setting additive	Degussa	2.19
Luminescent pigment extra fine	Pigment LumiNova°	Nemoto & Co. Ltd.	31.65
TOTAL			100

According to another aspect the present invention provides a method for preparing the above-defined

luminescent coatings. This method comprises a first step, wherein a base paste for the coating is prepared, after which the luminescent pigment is added to the base paste in a final preparation step. This is done by mixing the luminescent with the base paste through careful stirring so as to ensure that the crystal structure of the luminescent pigments will be retained.

An example of the preparation method is explained in detail hereafter.

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First of all, a binder dispersion is weighed in the mixing vessel. Then the defoaming agent, the dispersion additive and the flow additive are added while stirring slowly. Then the anti-setting additive is added, after 5 which it is dispersed to a fineness of < 5  $\mu m$  by means of a high-speed dispersion apparatus. The dispersion temperature must not rise above 60 °C, however. Following that, the thickener is added while stirring slowly but firmly. Once the thickener is homogeneously dispersed in the paint, check for clots, the luminescent pigment can be added while stirring carefully.

Another aspect of the present invention is the use of the luminescent coating for coating a light-transmitting or transparent surface, for example a lamp housing. 15

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Said use of a luminescent coating according to the present invention on a light-transmitting or transparent surface is already included in the Dutch patent application NL-A-1009136, which has not been published yet.

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#### CLAIMS

1. A luminescent coating comprising: a luminescent pigment of matrix formula MAl<sub>2</sub>O<sub>4</sub>, wherein M is at least one metal selected from the group comprising calcium, strontium and barium, or on the other hand of matrix MAl<sub>2</sub>O<sub>4</sub>, wherein M is a multitude of metal elements, comprising magnesium and at least one element selected from the group consisting of calcium, strontium and barium and a water-borne polyurethane binder dispersion and an anti-sagging additive.

- 2. A luminescent coating according to claim 1, wherein said anti-sagging additive is a hydrophobic pyrogenous silica.
  - 3. A luminescent coating according to claim 1 or 2, consisting of:
- 40 80 % by weight of water-borne polyurethane binder dispersion;
  - 19.5 59.5 % by weight of luminescent pigment;
  - 0.5 10 % by weight of anti-sagging additive;
  - 0 5 % by weight of further additives.

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- 4. A luminescent coating according to claim 3, wherein said further additives include a dispersion additive in an amount of 0.1 - 5 % by weight.
- 30 5. A luminescent coating according to claim 3 or 4, characterized in that said further additives are selected from the group consisting of a flow additive, a defoaming agent and a thickener.
- 35 6. A luminescent coating according to any one of the preceding claims, wherein said coating is diluted with N-methyl-2-pyrrolidone and water in a weight

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#### ratio of 1 : 12.

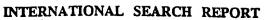
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- 7. A method suitable for preparing a luminescent coating according to any one of the preceding claims, wherein a base paste for the coating is prepared in a first step and the luminescent pigment is added to the base paste in a final step.
- A method according to claim 7, characterized in 8. 10 that the water-borne polyurethane binder dispersion is weighed in a first step, then the defoaming agent, the dispersion additive and the flow additive are added while stirring slowly, then the anti-setting additive is added in a next step by means of a high-speed dispersion apparatus and the 15 obtained mixture is stirred for a suitable period of time, using a suitable number of revolutions, whereby the temperature must not rise above 60 °C, after which the thickener is added while stirring, and in a final step the luminescent pigment is 20 added.
- Use of a luminescent coating according to any one of the claims 1 6 for coating a light-transmitting or transparent surface.
  - 10. Use according to claim 9, wherein said lighttransmitting or transparent surface is a lamp housing.

# INTERNATIONAL SEARCH REPORT ITAL BONAL Application No

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A. CLASSI IPC 7	FICATION OF SUBJECT MATTER C09K11/64 C09K11/02 C09D5/22				
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